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by John D. Clayton, Peter W. Chung, M. A. Grinfeld, and William D. Nothwang

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14. ABSTRACT
A model is developed for the electromechanical behaviour of dielectric crystals with defects: dislocations, vacancies, and misoriented boundaries. A geometric framework describes the deformation of the lattice in the presence of such defects. Thermodynamic and kinetic relations are formulated, the latter enabling description of diffusion of charged vacancies and mass rearrangement at free surfaces. Analytical and numerical solutions of specific problems offer insight into performance of barium strontium titanate (BST) films.

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CONTINUUM MODELING OF ELASTIC DIELECTRIC SOLIDS WITH DEFECTS, WITH APPLICATION TO BARIUM STRONTIUM TITANATE THIN FILMS

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Summary A model is developed for the electromechanical behaviour of dielectric crystals with defects: dislocations, vacancies, and misoriented boundaries. A geometric framework describes the deformation of the lattice in the presence of such defects. Thermodynamic and kinetic relations are formulated, the latter enabling description of diffusion of charged vacancies and mass rearrangement at free surfaces. Analytical and numerical solutions of specific problems offer insight into performance of barium strontium titanate (BST) films.

THEORY: KINEMATICS, THERMODYNAMICS, AND KINETICS

A number of continuum theories describing the coupled electrostatic and mechanical behaviour of dielectric crystalline solids have emerged during the previous half century [1-3]. The present formulation extends traditional models [2] of elastic dielectric materials to account for imperfections in the lattice, specifically vacancies and dislocations. Effects of misorientations across polarized subdomains are also considered. Defects are not resolved individually, but instead their number densities are treated via continuous distributions. The macroscopic displacement gradient $\nabla\mathbf{u}$ obeys

$$\nabla\mathbf{u} = \boldsymbol{\gamma}^E + \boldsymbol{\gamma}^P + \boldsymbol{\gamma}^V, \qquad \dot{\boldsymbol{\gamma}}^P = \sum_k \nu^{(k)}\mathbf{s}^{(k)} \otimes \mathbf{m}^{(k)}, \qquad \boldsymbol{\gamma}^V = (\chi/3)\mathbf{1}, \tag{1}$$

where $\boldsymbol{\gamma}^E$ is the recoverable lattice distortion, $\boldsymbol{\gamma}^P$ is the plastic distortion, $\boldsymbol{\gamma}^V$ is expansion or contraction from defects, ν is the slip rate on glide system k with direction $\mathbf{s}$ and normal $\mathbf{m}$, and χ is the volume fraction of defects. Let

$$\dot{\xi} = -\nabla\bullet\mathbf{Q}, \qquad \chi = \alpha\xi, \qquad \dot{a} = -\alpha(\mathbf{Q}\bullet\mathbf{n} + \bar{\nabla}\bullet\mathbf{q})/(1 - tr\boldsymbol{\gamma}^{\mathbf{E}} - \chi), \tag{2}$$

where $\mathbf{Q}$ is the bulk flux of vacancies, ξ is the number of vacancies per unit volume, and α is the volume per vacancy. Surface fluxes are described by the vector $\mathbf{q}$, with components spanning two surface coordinates, and $\bar{\nabla}$ is the surface gradient. Conservation of mass at external surface s provides the final equality in (2) specifying the rate of surface growth $\dot{a}$ [4]. The lattice deformation mapping $\mathbf{A}$ is introduced similarly to that in [5]:

$$A^a_{\cdot b} = \delta^a_{\cdot b} + \gamma^{Ea}_{\cdot\cdot b} + \gamma^{Va}_{\cdot\cdot b}, \qquad \hat{\nabla}_b\mathbf{d}_a = \mathbf{d}_{a,b} - \hat{\Gamma}^{\cdot\cdot c}_{ba}\mathbf{d}_c, \qquad \hat{\Gamma}^{\cdot\cdot a}_{cb} = A^a_d A^{-1d}_{\cdot\cdot b,c} + \Xi^{\cdot\cdot a}_{cb} + \Upsilon_c\delta^{\cdot a}_b, \tag{3}$$

and includes effects of elasticity and stress-free volumetric expansion, but not dislocation glide. Spatial gradients on the manifold of lattice directors $\mathbf{d}_a$ are described by the covariant derivative $\hat{\nabla}$ [5, 6], where $\Xi^{\cdot\cdot a}_{cb}$ and Υ_c account for rotation and stretch gradients, respectively, due to surface and point defects. Three quantities describing the defect content of the crystal emerge from the torsion and curvature of the connection in the second and third of Eq. (3): the dislocation density tensor, the disclination density tensor, and the point defect vector, each having physical interpretations in perovskite crystals. The local governing equations of electrostatics are written in reduced form as [1, 2]

$$\mathbf{E} = -\nabla\phi, \qquad \hat{\rho} = \nabla\bullet\mathbf{D}, \qquad \mathbf{D} = \varepsilon_0\mathbf{E} + \mathbf{P}, \tag{4}$$

with $\mathbf{E}$ the electric field, ϕ the electric potential, $\mathbf{D}$ the electric displacement, $\mathbf{P}$ the polarization, ε_0 the permittivity of free space, and $\hat{\rho}$ the charge density related to the concentration of vacancies by $\hat{\rho} = ez\xi$, where e is the charge of an electron and z is the valence contribution of each defect. The Helmholtz free energy per unit mass follows the functional dependencies

$$\psi = \psi(\boldsymbol{\gamma}^{\mathbf{E}}, \mathbf{P}, \xi, h, \theta), \tag{5}$$

with the scalar-valued function h accounting for energetic contributions from point, line, and surface defects distinct from ξ. An admissible set of bulk thermodynamic and kinetic relations is

$$\sigma^{ab} = \rho\partial\psi/\partial\gamma^E_{(ab)}, \qquad E_a = \rho\partial\psi/\partial P^a, \qquad \eta = -\partial\psi/\partial\theta, \tag{6}$$

$$\mu = \rho\partial\psi/\partial\xi + ez\phi + \alpha p, \qquad \mathbf{Q} = -\mathbf{d}\bullet\nabla\mu, \qquad \sum\tau^{(k)}\nu^{(k)} + \nabla\mu\bullet\mathbf{d}\bullet\nabla\mu \geq \dot{h}\rho\partial\psi/\partial h, \qquad |\mathbf{d}| \geq 0. \tag{7}$$

Above, $\boldsymbol{\sigma}$ is the stress, ρ is the mass density, η is the entropy, p is the pressure, $\mathbf{d}$ is the bulk diffusivity of point defects, and $\tau^{(k)}$ is the resolved shear stress on slip system k. At free surfaces, vacancy fluxes obey

$$\mathbf{Q}\bullet\mathbf{n} = \beta\left[\alpha\left(\rho\psi + \phi\hat{\rho} - \kappa\varsigma\right)/\left(1 - tr\boldsymbol{\gamma}^{\mathbf{E}} - \chi\right) + \mu\right], \quad \mathbf{q} = -\hat{\mathbf{A}}\bullet\overline{\nabla}\left[\left(\rho\psi + \phi\hat{\rho} - \kappa\varsigma\right)/\left(1 - tr\boldsymbol{\gamma}^{\mathbf{E}} - \chi\right)\right], \quad \left|\hat{\mathbf{A}}\right| \geq 0, \quad (8)$$

where ς is the energy per unit area associated with surface tension, κ is the surface curvature, and $\beta \geq 0$. Extension of the theory to large deformations and nonlinear electrostatics is currently underway.

APPLICATION: CHARGED VACANCY MIGRATION IN BST THIN FILMS

The present application focuses on BST films in the paraelectric (i.e. cubic) phase. Free energy potential (8) is written

$$\rho\psi = \mathbb{C}^{abcd}(1 - \alpha\xi)\gamma^{E}_{(ab)}\gamma^{E}_{(cd)}/2 + \Lambda_{ab}P^{a}P^{b}/2 + \varphi, \quad (9)$$

$$\varphi = \alpha^{-1}N_{A}(G_{0}(\theta) + N_{A}k_{B}\theta\chi\ln\chi) \approx \alpha^{-1}N_{A}(G_{0}(\theta) + \Gamma N_{A}k_{B}\theta\chi^{2}/2), \quad (10)$$

where $\mathbb{C}^{abcd}$ and Λ_{ab} are elastic and dielectric constants, respectively, and where N_A and k_B are Avogadro's number and Boltzmann's constant. Equations (2), (3), and (6)-(8) are solved using numerical methods (1-D and 3-D transient simulations) and analytical methods (1-D steady-state solutions). In the former case, in one spatial dimension (Fig. 1) and under the action of an externally applied voltage, vacancies coalesce into layers of large concentration near potential free boundaries when the first of (10) is used, leading to an increase in the electric field in the vicinity of such boundaries that may affect loss characteristics of the film. Heterogeneous growth of the surface of the film resulting from surface roughness is evident in the 3-D solution of (2) and (8), as shown in Fig. 2. At steady state and in one spatial dimension, using the second of (10), the vacancy distribution obeys the simple equation

$$(\Gamma k_{B}\theta + 2\alpha\mathbb{C}\gamma^{E}/3)d^{2}\chi/dx^{2} - (ez)^{2}(\alpha\varepsilon_{0}\varepsilon_{R})^{-1}\chi = 0, \quad (11)$$

where $\mathbb{C}$, γ^{E}, and ε_{R} are respectively the elastic modulus, uniaxial elastic strain, and dielectric constant. The solution of (11) for boundary conditions corresponding to a grain boundary depletion layer [7] is shown in Fig. 3, where $\bar{\sigma}$ is the average compressive residual stress in the film possibly due to interfacial lattice parameter mismatch, σ' and Γ' are the normalized stress and normalized energy per vacancy, and χ_S is the saturation density of vacancies. Nonlinear defect distributions and decreasing average concentration are positively correlated with increasing compressive stresses.

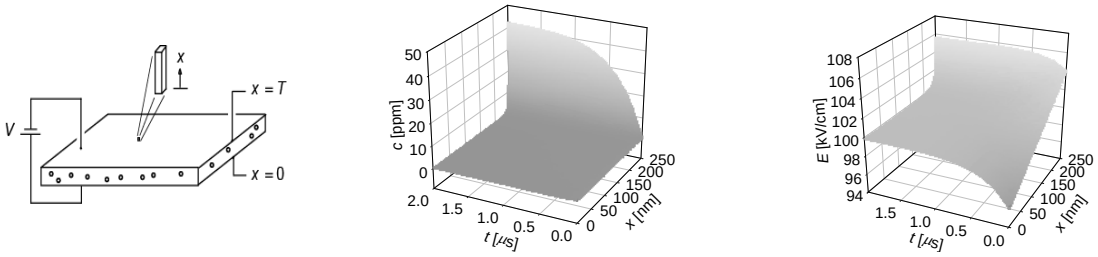

Fig. 1. Numerical solution (1-D) for BST film of thickness T: (left) geometry, (center) transient vacancy concentration c, and (right) electric field E (initial concentration $c_0 = 0.5$ ppm, applied voltage $V = \phi_{x=0} = 2.5$ V).

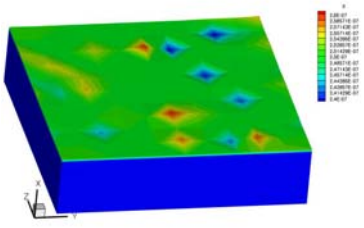

Fig. 2. Numerical solution (3-D) for surface coordinate x.

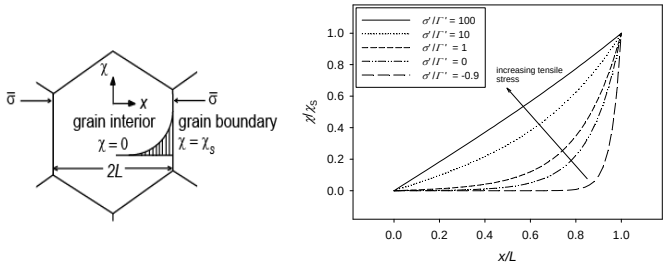

Fig. 3. Geometry and analytical solution (1-D) for steady state vacancy content.

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